

THERMODYNAMICS AND SPECTROSCOPIC ANALYSIS OF PURE AND MIXED GAS HYDRATES FORMED IN POROUS MEDIA

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ABSTRACT

Three-phase H-L_w-V equilibria for the binary CO₂ + water mixtures in silica gel pores with nominal diameters of 6.0, 15.0 and 30.0 nm were measured. In addition, the hydrate phase equilibria of the ternary CO₂ + NaCl + water mixtures were measured in 15.0 nm silica gel pores at three different NaCl concentrations of 3, 5, and 10 wt% to secure fundamental electrolyte role on simple hydrate formation occurring within porous media. The hydrate phase equilibria of the CH₄ + CO₂ + water mixture in 15.0 nm silica gel pores were also carefully determined at CO₂ compositions of 20, 40, 60, and 80 mol% in order to meet changeable surroundings of sea floor and sediments. The three different silica gels of nominal diameters 6.0, 15.0 and 30.0 nm were used to check pore-size effects on hydrate equilibrium. All these measured data were compared with calculated values based on the van der Waals and Platteeuw model incorporated with two additional terms considering the effect of electrolytes and pores. Finally, to check the possible structure transition and the pore size effect on composition change the crystalline structure and hydration number of hydrates formed in silica gel pores of various sizes were identified by using the ¹³C NMR.

KEY WORDS: carbon dioxide, clathrate, hydrate, NMR, phase equilibria

1. INTRODUCTION

Gas hydrates are of particular interest in the petroleum industry as well as in energy and environmental field. Initial interest in gas hydrates began with the discovery that hydrate formation could plug natural gas pipelines. Large masses of natural gas hydrates exist both on-shore buried under the permafrost and off-shore buried under the oceanic and deep lake sediments. Recent investigations consider the possibility of sequestering industrially produced carbon dioxide as crystalline gas hydrates in the deep ocean to prevent further release into the atmosphere as greenhouse gas. It has been also investigated that the injection of CO_2 into CH_4 hydrate reserves could result in simultaneous process merits of both CO_2 sequestration and CH_4 exploitation[1]. Since these natural phenomena of hydrate formation/substitution occur in deep ocean sediments, it becomes essential to consider the complicated effects of both porous media and electrolytes on the formation of simple and mixed hydrates.

Handa and Stupin[2] first studied the effect of porous media on equilibrium pressures of CH_4 and C_3H_8 hydrates. They showed that the equilibrium pressures of CH_4 and C_3H_8 hydrates in silica gel pores were higher than those of the bulk hydrates. Uchida et al.[3,4] experimentally determined the equilibrium pressures of CH_4 , C_3H_8 and CO_2 hydrates in porous glasses of different pore sizes. Seshadri et al.[5] and Smith et al.[6] reported the pore equilibrium pressure-temperature data of C_3H_8 and CH_4 hydrates, respectively, in silica gels by using the same experimental method suggested by Handa and Stupin[2]. Recently, Wilder et al.[7], Klauda and Sandler[8], and Smith et al.[6]also proposed the calculation methods considering the pore-size distributions because the large discrepancies between the experimental values of Handa and Stupin [2]and calculated ones of Henry et al.[9] and Clarke et al.[10] might be attributed to the assumption of single pore size. However, the pore hydrate equilibrium data experimentally determined and particularly approaching the lower quadruple point were not consistent with the generally expected phase behavior and therefore there existed a difficulty for developing the proper pore hydrate model. In this study, to confirm and overcome the inconsistency between experimental and model values, the equilibrium dissociation pressures for CO_2 hydrates confined in silica gel pores of nominal diameters 6.0, 15.0 and 30.0 nm were carefully measured and compared with the proposed model calculations considering the interfacial tension between hydrate and liquid water phases for capillary effect.

The cage substitution mechanism between CH_4 and CO_2 molecules might be thought to be easily tractable, but for its complete understanding both equilibrium and nonequilibrium approaches are required in the bulk and porous medium surroundings.

Moreover, the highly complex phase behavior of mixed hydrate systems containing multi-guest components must be explored *a priori* to examine the feasibility of natural gas exploitation in connection with CO₂ sequestration. In this connection, the present work was newly attempted to provide fundamental key information of electrolyte effects on hydrate phase equilibrium behavior, particularly, in porous media. The hydrate phase equilibria of the ternary and CO₂ + NaCl + water mixtures were measured in 15.0 nm silica gel pores at three different NaCl concentrations of 3, 5, and 10 wt% to secure fundamental electrolyte role on simple hydrate formation occurring in pores. The hydrate phase equilibria of the CH₄ + CO₂ + water mixture in 15.0 nm silica gel pores were also carefully determined at CO₂ compositions of 20, 40, 60, and 80 mol% in order to meet changeable surroundings of sea floor and sediments. The three different silica gels of nominal diameters 6.0, 15.0 and 30.0 nm were used to check pore-size effects on hydrate equilibrium. All these measured data were compared with calculated values based on the van der Waals and Platteeuw model incorporated with two additional terms considering electrolytes and pores. Finally, to check the possible structure transition and the pore size effect on composition change the crystalline structure and hydration number of hydrates formed in silica gel pores of various sizes were identified by using the ¹³C NMR.

2. EXPERIMENTAL

2.1. Hydrate Phase Equilibria

CO₂ gas of 99.9 mol% purity was supplied by World Gas (Korea) and CH₄ gas with a minimum purity of 99.95 mol % by Linde Gas UK Ltd (UK). The CH₄ + CO₂ gas mixtures (20, 40, 60, 80 mol% CO₂) were supplied by World Gas (Korea) and ¹³CH₄ gas of 99.0 mol% purity by Cambridge Isotope Laboratories (USA). The water with ultra high purity was supplied from Merck (Germany). Silica gels of nominal pore diameter 6.0 nm (6.0 nm SG) and 15.0 nm (15.0 nm SG) were purchased from Aldrich (USA) and 30.0 nm silica gel (30.0 nm SG) from Silicycle (Canada). All materials were used without further treatment. The properties of silica gels having three different pore diameters were measured by ASAP 2000 (Micromeritics, USA) and listed in Table 1. Their pore-size distributions were also determined and shown in Figure 1. The used silica gels were first dried at 373 K for 24 h before water sorption. Then, the pore saturated silica gels were prepared by placing these dried silica gels in a desiccator containing degassed and distilled water, evacuating the desiccator and allowing more

than 5 days in order to establish the solid-vapor equilibrium. The total amount of sorbed water in the silica gel pores was confirmed by measuring the mass of silica gels before and after saturation and found to be almost identical with the pore volume of each silica gel. For silica gels containing NaCl solution, we followed the same method suggested by Uchida et al.[3]. The amount of electrolyte solution equivalent to total pore volume of dried silica gels was added to the sample contained in the bottle. After being mixed, the mixture was sealed off with a cap to prevent water evaporation. In order to facilitate water filling into the pores, the bottle with the mixture was vibrated and warmed up for 24 h with an ultrasonic wave. The validity of this method was verified by comparing the experimental results obtained from two different methods.

A schematic diagram of the experimental apparatus for hydrate phase behavior is given in Figure 2. The apparatus was specially constructed to measure accurately the hydrate dissociation pressures and temperatures. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 50 cm³. The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 25 cm³ of silica gels containing pore water. After the equilibrium cell was pressurized to a desired pressure with gas, the whole main system was slowly cooled to 263 K. When pressure depression due to hydrate formation reached a steady-state condition, the cell temperature was increased at a rate of about 0.1 K/h. The nucleation and dissociation steps were repeated at least two times in order to reduce hysteresis phenomenon. The equilibrium pressure and temperature of three phases (hydrate (H) - water-rich liquid (L_w) - vapor (V)) were determined by tracing the *P-T* profiles from hydrate formation to dissociation. Unlike the bulk hydrate, in case of hydrates in silica gel pores, a gradual change of slope around the final hydrate dissociation point was observed due to the pore-size distribution. As a consequence, it becomes, of course, very difficult to determine the unique equilibrium dissociation point in the *P-T* profile measured for the silica gel pores. To overcome this inherent difficulties the dissociation equilibrium point in silica gel pores was chosen in the present study as the cross point between the maximum inclination line and complete dissociation line (Figure 3). As indicated by Uchida et al.[3], this unique point corresponds to the dissociation one in the pores of the mean diameter of used silica gels.

2.2. Spectroscopic Analysis

To identify crystalline structure and hydration number of CH₄ and CH₄ + CO₂ hydrates formed in silica gel pores and compare them with those of CH₄ hydrate formed in bulk state, a Bruker 400 MHz solid-state NMR spectrometer was used in this study.

The NMR spectra were recorded at 200 K by placing the hydrate samples within a 4 mm o.d. Zr-rotor that was loaded into the variable temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 2-4 kHz. The pulse length of 2 μs and pulse repetition delay of 20 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. The down-field carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. For the mixed hydrate samples of higher CO_2 compositions over 80 mol%, $^{13}\text{CH}_4$ gas was used to obtain much higher resolution of CH_4 peaks.

3. RESULTS AND DISCUSSION

3.1. Hydrate Phase Equilibria

Three-phase H-L_W-V equilibria of CO_2 hydrates confined in silica gel pores with nominal diameters 6.0, 15.0 and 30.0 nm were measured between lower and upper quadruple point temperatures. hydrate equilibrium data of the binary CO_2 + water mixtures were presented along with model calculations in Figure 4. Figure 4 also includes the hydrate equilibrium data obtained by Uchida et al. [4] for 30.0 nm pores. Although the experimental determinations of the binary CO_2 + water mixtures in porous silica gels were restricted to the H-L_W-V phase boundary, the model calculation could be extended to two different three-phase boundaries of hydrate (H) - ice (I) - vapor (V) and hydrate (H) - water-rich liquid (L_W) - carbon dioxide-rich liquid (L_{CO₂}). The upper quadruple points (Q₂) where two H-L_W-V and H-L_W-L_{CO₂} phase boundaries intersect and thus four phases (H, L_W, L_{CO₂} and V) coexist were located very closely along the saturation vapor pressure curve of CO_2 . In addition, the apparent equilibrium pressure shifts representing the equilibrium pressure difference between pore and bulk hydrates at a specified temperature were shown in Figure 5. As the pore size decreases and equilibrium temperature increases, the equilibrium pressure shifts were found to be larger.

Three-phase H-L_W-V equilibria for the ternary CO_2 + NaCl + water mixtures in 15.0 nm silica gel pores were measured at the NaCl concentration ranges of 3-10 wt% and presented along with model calculations in Figures 6. As expected, the presence of either geometrical constraints or electrolytes caused the H-L_W-V curves to be shifted more to inhibition region represented by the lower temperature and higher pressure

condition when compared with the ones in the either bulk or pure state. However, in the present work the combined effects of porous media and electrolytes that closely simulate real marine sediments were examined through checking the shift of the experimentally measured H-L_W-V curve.

Three-phase H-L_W-V equilibria for the ternary CH₄ + CO₂ + water mixtures of various CO₂ vapor compositions (20, 40, 60 and 80 mol %) in 15.0 nm silica gel pores were also measured and presented along with model calculations in Figure 7. As generally expected, the H-L_W-V lines of the ternary CH₄ + CO₂ + water mixtures existing between those of the binary CH₄ + water and CO₂ + water mixtures showed the pore inhibition. In particular, three-phase H-L_W-V equilibria for the ternary CH₄ + CO₂ + water mixtures of 40 mol % CO₂ in silica gel pores of nominal diameters 6.0, 15.0 and 30.0 nm were represented along with model calculations in Figure 8. The decrease of pore diameter made the H-L_W-V equilibrium line more shifted toward higher pressure region at a specified temperature.

3.2. Spectroscopic Analysis

For the CH₄ hydrate (CH₄ · *n* H₂O), the hydration number, *n*, has been determined by various calorimetric and spectroscopic methods[11,12]. However, in the present study, the NMR spectroscopy was adopted to determine the hydration numbers of CH₄ hydrates confined in silica gel pores because the NMR spectroscopy has been recognized as a powerful tool for identifying hydrate structures and compositions, determining guest and host dynamics, and monitoring hydrate formation kinetics[13]. Figure 9 shows a stacked plot of ¹³C MAS NMR spectra of CH₄ hydrates in porous silica gels and bulk state. All the spectra demonstrated two peaks at the same chemical shifts of -6.9 and -4.6 ppm, respectively. Since the ideal stoichiometric ratio of the small 5¹² to the large 5¹²6² cages in the unit cell of structure I is 1:3, the peak at -4.6 ppm can be assigned to CH₄ molecules in the small 5¹² cages and the peak at -6.9 ppm to CH₄ molecules in the large 5¹²6² cage.

CH₄ and CO₂ are each known to form sI hydrate. CO₂ is very hard to analyze quantitatively using NMR due to its molecular characteristics, so in the present study we focused only on the CH₄ molecules in the hydrate cages. Figure 4-11 shows a stacked plot of ¹³C MAS NMR spectra of CH₄ +CO₂ mixed hydrates of various CO₂ compositions in 15.0 nm silica gel pores. Since all the spectra demonstrated two peaks at the same chemical shifts of -6.9 and -4.6 ppm, respectively, it could be confirmed that the structure transition did not occur for the CH₄ + CO₂ mixed hydrates of various CO₂ compositions. In Figure 10, it can be seen that the area ratios of large to small cages of

CH₄ peaks become smaller as the CO₂ compositions of initial vapor phase increase. This behavior can be explained in terms of molecular sizes of CO₂ and CH₄. The molecular size of CO₂ is almost the same as the cavity diameter of small 5¹² cage in sI hydrate; molecular diameter/cavity diameter = 1.00 for CO₂, 0.855 for CH₄[14]. Because of the relative sizes of CO₂ molecule and small 5¹² cage in sI hydrate, it was assumed that the small 5¹² cage was essentially unoccupied by CO₂. However, some recent investigations from NMR and XRD show that CO₂ can also occupy the small 5¹² cage of sI hydrate to some extent[15,16]. When CO₂ competes with CH₄ in occupying the small cage of sI hydrate, CO₂ is relatively poor guest for small 5¹² cage. Accordingly, occupancy ratio for CH₄ ($\theta_{L,CH_4}/\theta_{S,CH_4}$) was found to be lower at higher CO₂ compositions because CO₂ preferentially occupied the large 5¹²6² cage of CH₄ + CO₂ mixed hydrates.

In Figure 11, area ratios of large to small cage of CH₄ peaks ($A_{L,CH_4}/A_{S,CH_4}$) were expressed along with occupancy ratio ($\theta_{L,CH_4}/\theta_{S,CH_4}$) after considering that there are three times as many large 5¹²6² cage as small 5¹² one in sI hydrate. Pure CH₄ hydrate in 15.0 nm silica gel pores gave the value of 3.77 for $A_{L,CH_4}/A_{S,CH_4}$ which corresponds to the hydration number of 6. 19 and $\theta_{L,CH_4}/\theta_{S,CH_4}$ of 1.26. From Figure 11, the value of $\theta_{L,CH_4}/\theta_{S,CH_4}$ at 100 mol% CO₂ can be inferred through extrapolation and this hypothetical value which means competitiveness of CH₄ molecules with CO₂ ones at infinite dilution of CH₄ was found to be about 0.23.

4. CONCLUSION

Three-phase H-L_W-V equilibria for the binary CO₂ + water mixtures in silica gel pores with nominal diameters of 6.0, 15.0 and 30.0 nm were measured and compared with the pore hydrate model calculations. In addition, three-phase H-L_W-V equilibria for the ternary CO₂ + NaCl + water mixtures in 15.0 nm silica gel pores and for the ternary CH₄ + CO₂ + water mixtures of various CO₂ compositions in silica gel pores with nominal diameters of 6.0, 15.0 and 30.0 nm were also measured and compared with model calculations. The presence of geometrical constraints and electrolytes made H-L_W-V equilibrium lines shifted to higher pressure region at a specified temperature. A

Pitzer model for electrolytes solutions and a correction term for capillary effect were adopted to estimate the activity of water in the aqueous electrolyte solutions within silica gel pores. By using the values of interfacial tension between hydrate and liquid water phases which were recently presented by Uchida et al.⁵, the resulting accuracies and overall H-L_w-V trend particularly approaching the H-I-V line obtained from the present pore hydrate model were greatly improved both quantitatively and qualitatively. The structures of CH₄ and CH₄ + CO₂ mixed hydrates formed in silica gel pores were confirmed to be identical with those of bulk CH₄ hydrate through ¹³C NMR spectroscopy. Furthermore, the pore hydration number was found to be almost constant for all pore sizes. The overall thermodynamic and spectroscopic results drawn from the present study can be used for understanding the fundamental phase behavior and structure details of pore hydrates and thus, could be applied as a valuable key information to developing the natural gas hydrate in marine sediments and sequestering carbon dioxide into the deep ocean.

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Table I. Physical properties of silica gel samples

Sample	6.0 nm SG	15.0 nm SG	30.0 nm SG
mean particle diameter (μm)	(33-74)	(33-74)	(40-75)
mean pore diameter (nm)	6.8 (6.0)	14.6 (15.0)	30.5 (30.0)
pore volume (cm^3/g)	0.84 (0.75)	1.13 (1.15)	1.17 (-)
surface area (m^2/g)	497 (480)	308 (300)	111 (100)

*Values in the parenthesis are vendor data.

Figure Captions

Fig. 1. Pore-size distribution of silica gels used in this study.

(a) 6.0 nm (b) 15.0 nm (c) 30.0 nm

Fig. 2. Experimental apparatus for hydrate phase equilibria.

Fig. 3. P-T trace for determination of final equilibrium dissociation point (15.0 nm SG).

Fig. 4. Hydrate phase equilibria of the binary CO_2 + water mixtures in silica gel pores.

Fig. 5. Equilibrium pressure shifts between pore and bulk hydrate for CO_2 hydrate

Fig. 6. Hydrate phase equilibria of the ternary CO_2 + NaCl + water mixtures in 15.0 nm silica gel pores.

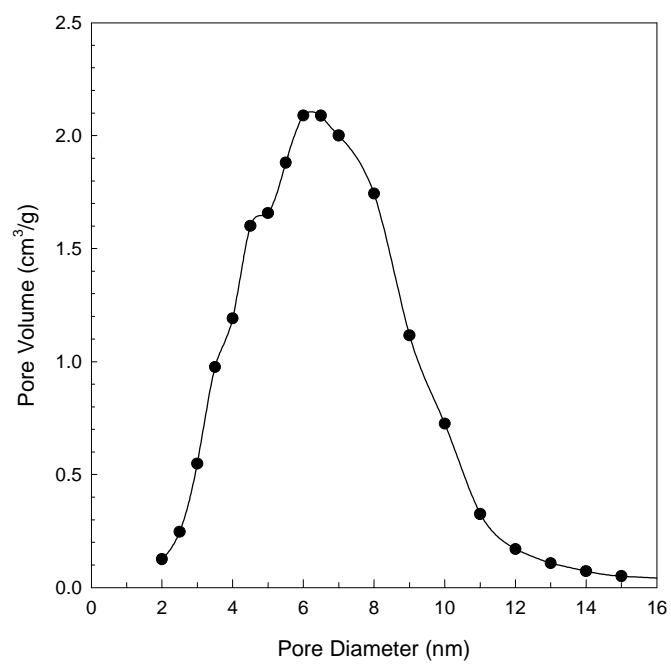
Fig. 7. Hydrate phase equilibria of the ternary CH_4 + CO_2 + water mixtures of various CO_2 compositions (20, 40, 60 and 80 mol%) in 15.0 nm silica gel pores.

Fig. 8. Hydrate phase equilibria of the ternary CH_4 + CO_2 + water mixtures of 40 mol% CO_2 in silica gel pores (6.0, 15.0 and 30.0 nm).

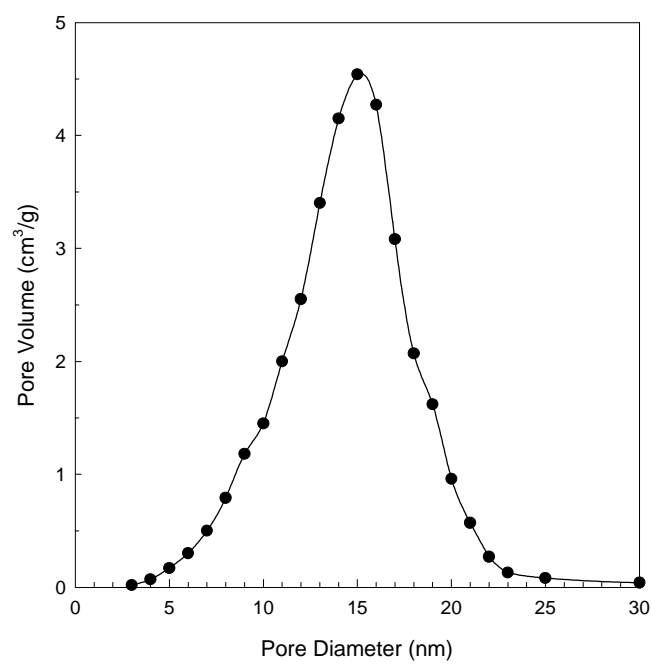
Fig. 9. ^{13}C NMR spectra of CH_4 hydrates in silica gel pores and bulk state at 200 K.

Fig. 10. ^{13}C NMR spectra of CH_4 + CO_2 mixed hydrates in 15.0 nm silica gel pores at 200 K.

Fig. 11. Area ratio of large $5^{12}6^2$ to small 5^{12} cages of CH_4 peaks in CH_4 + CO_2 mixed hydrates formed in 15.0 nm silica gel pores.



(a)



(b)

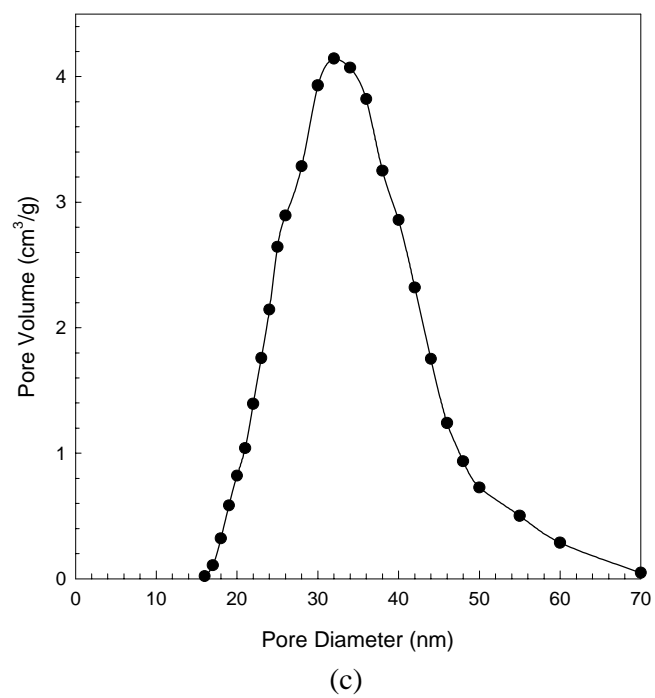


Fig. 1

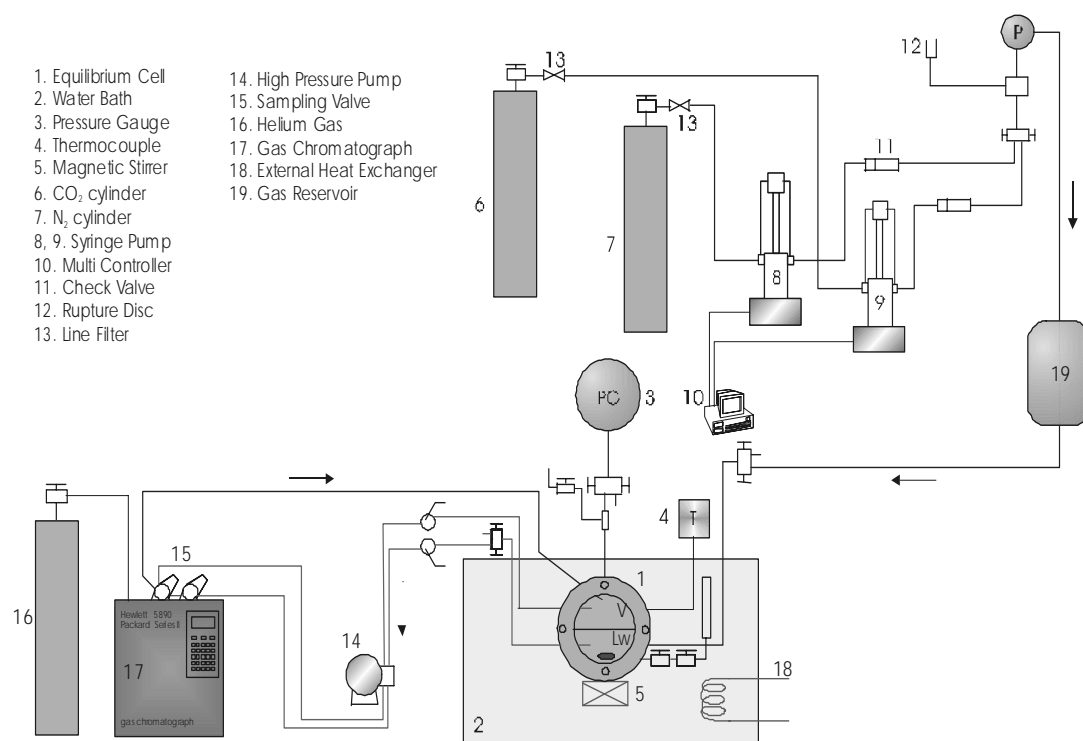


Fig. 2

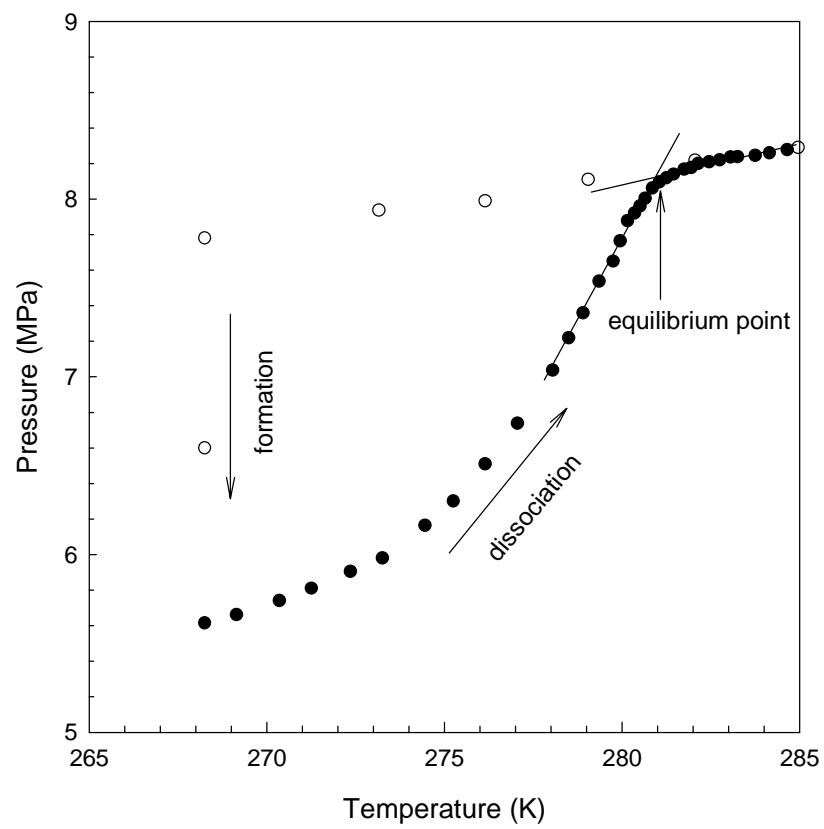


Fig. 3

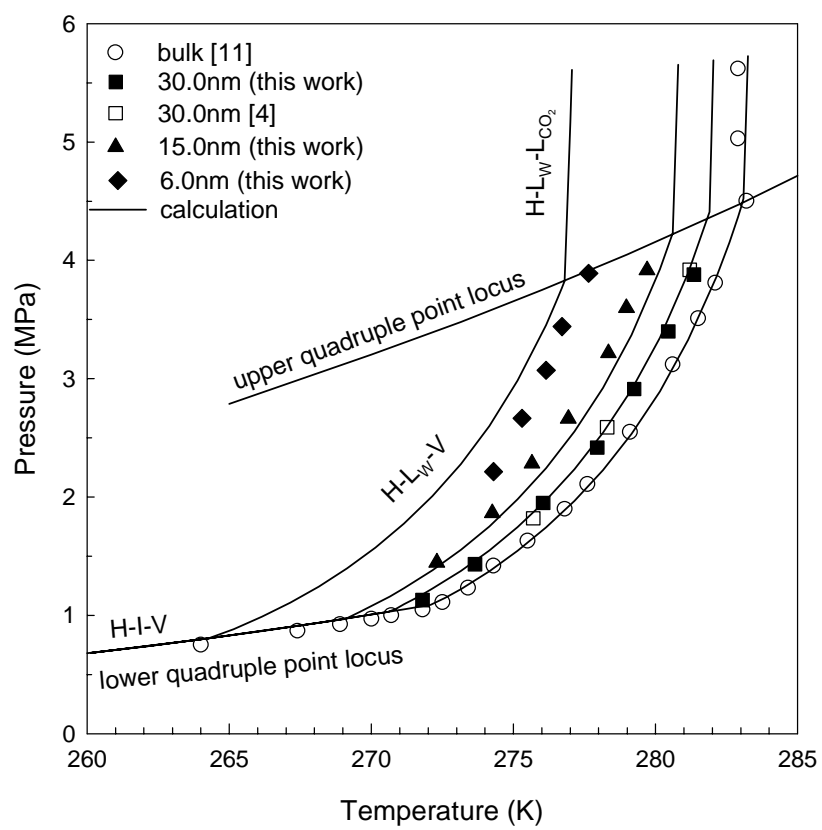


Fig. 4

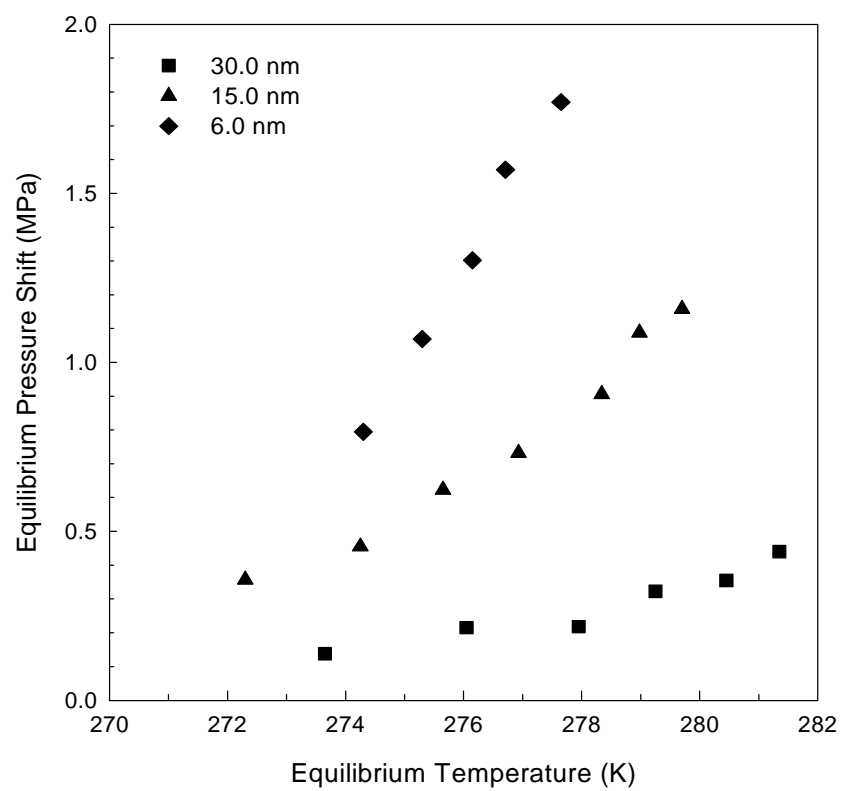


Fig. 5

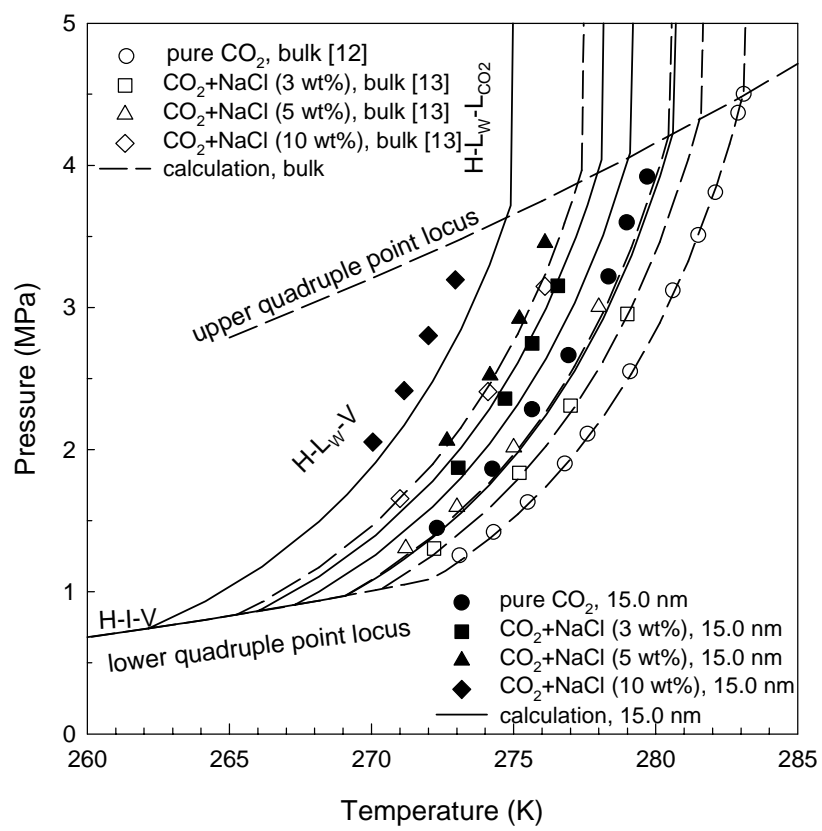


Fig. 6

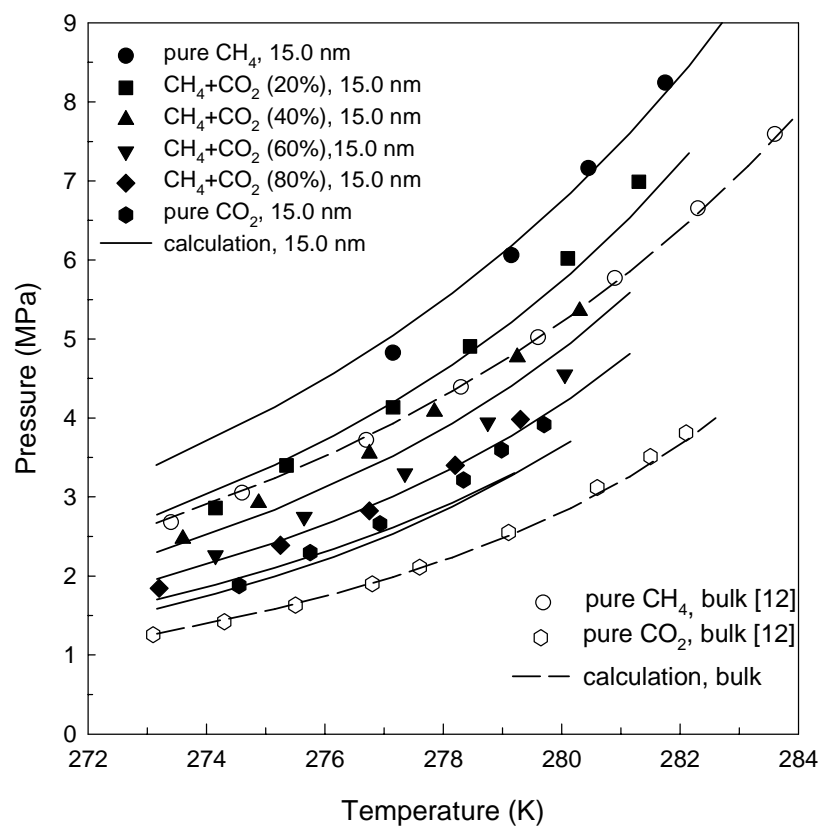


Fig. 7

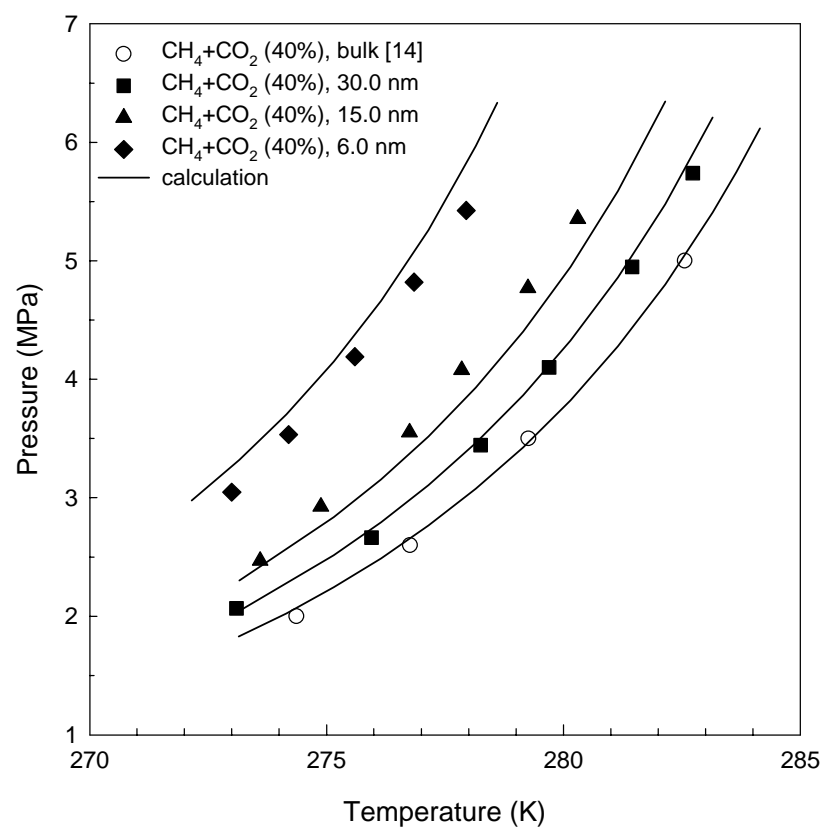


Fig. 8

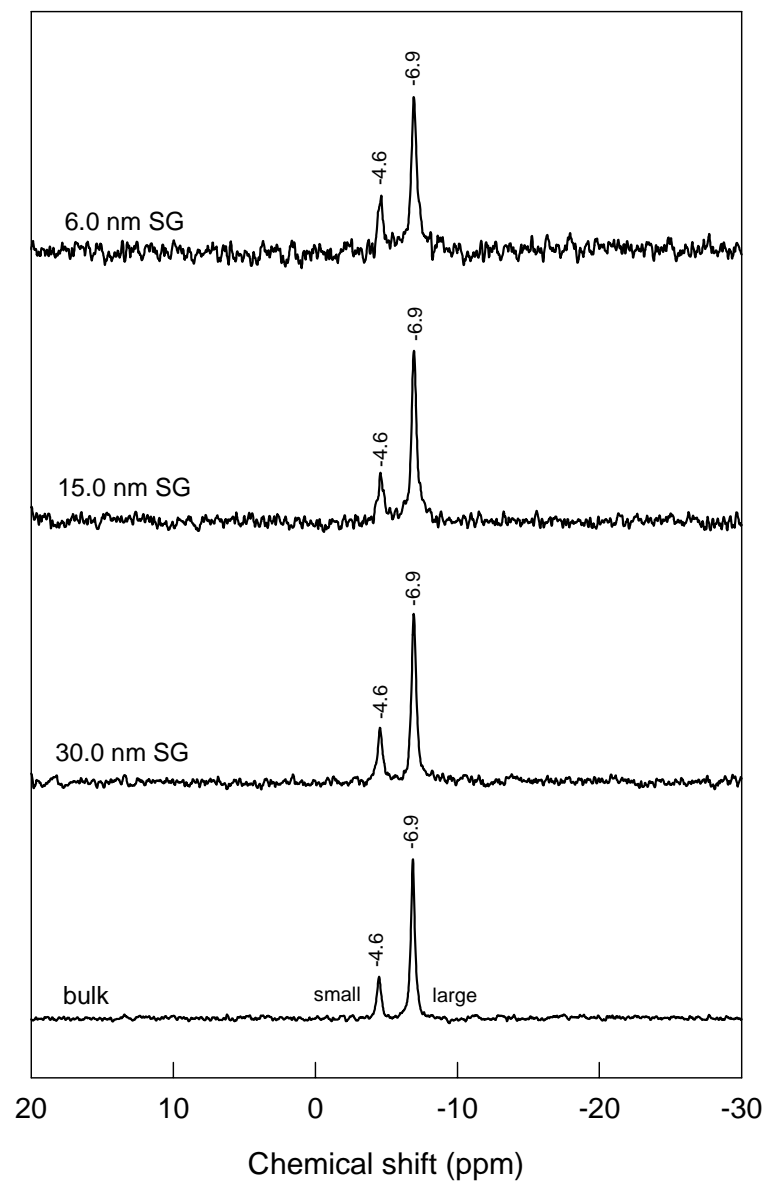


Fig. 9

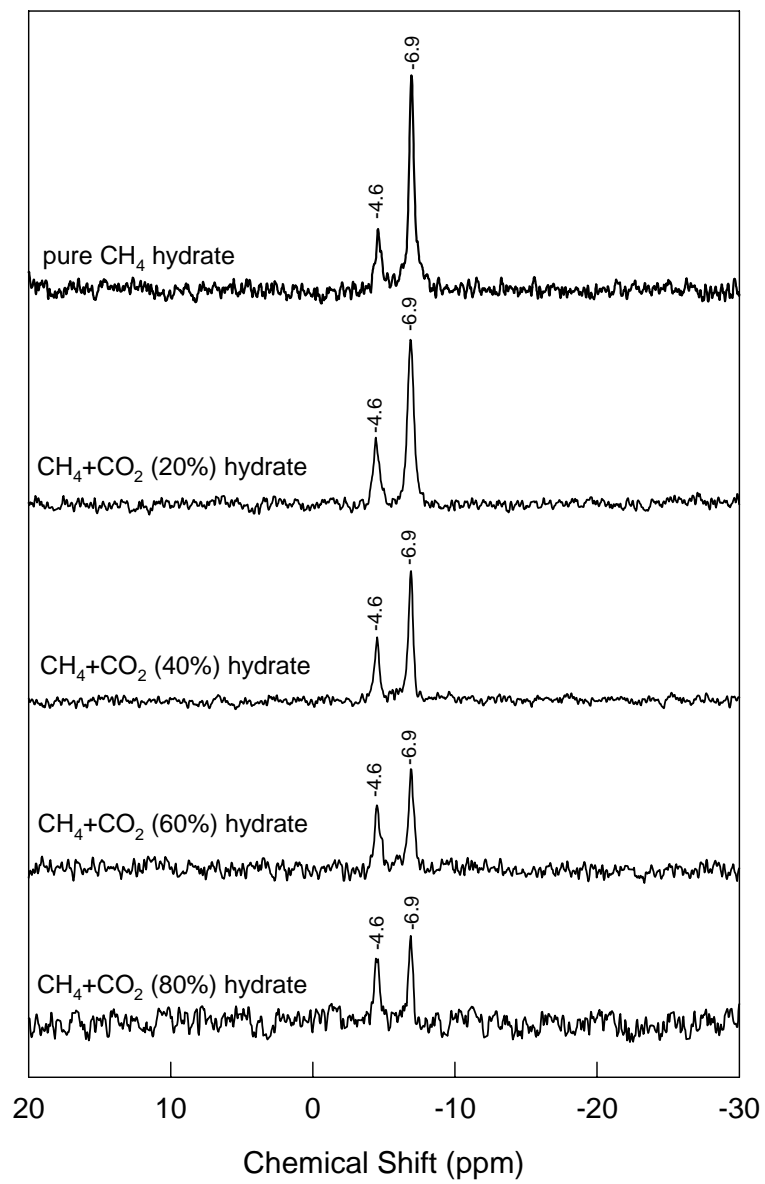


Fig. 10

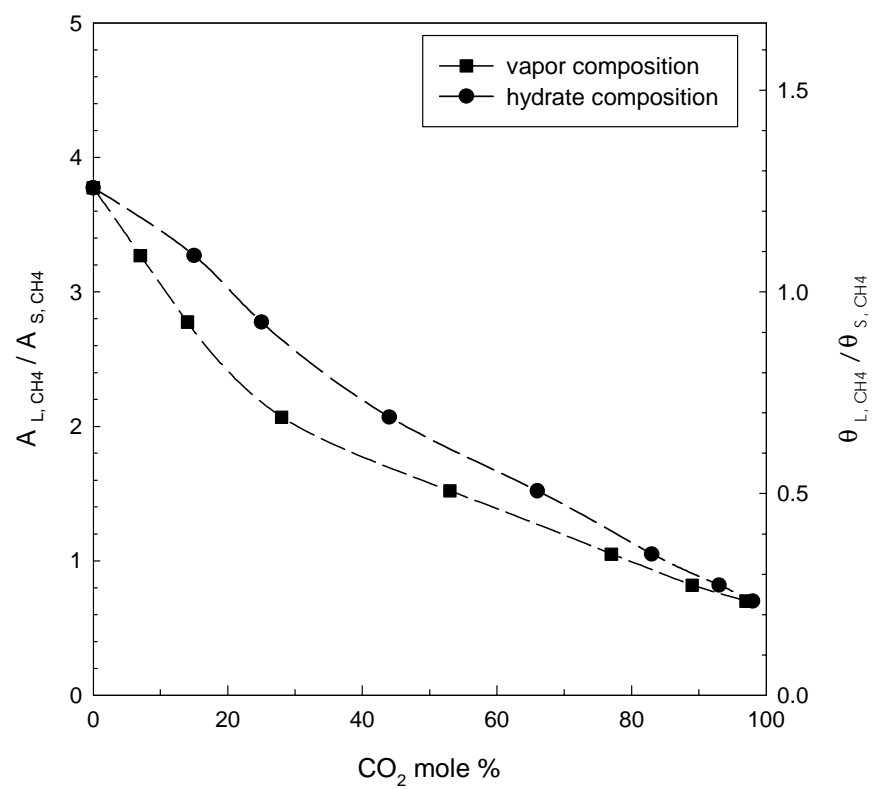


Fig. 11